Electrostatic field in a pseudo-cubic ionic structure. Application to all BaTio3 structure-types

C. Tsallis, R. Machet, J. Bouillot

To cite this version:

HAL Id: jpa-00207039
https://hal.archives-ouvertes.fr/jpa-00207039
Submitted on 1 Jan 1971
ELECTROSTATIC FIELD IN A PSEUDO-CUBIC IONIC STRUCTURE.
APPLICATION TO ALL BaTiO₃ STRUCTURE-TYPES

by C. TSALLIS (*)

Laboratoire de Magnétisme et Physique des Solides C. N. R. S. Bellevue/Meudon

R. MACHET and J. BOUILLOT

Laboratoire de Diélectriques-Ferroélectriques, Faculté des Sciences, Dijon

(Reçu le 17 septembre 1970)

Résumé. — Description d'une méthode générale de calcul du champ électrostatique au voisinage de chaque point de symétrie d'un sous-réseau cristallin pseudo-cubique quelconque dont les sites sont occupés par des charges identiques. Une superposition de sous-réseaux de ce type peut être, pour certains calculs statiques et dynamiques (en particulier dans le cadre du modèle de couches), une image utile d'un cristal ionique. Le champ est développé au 3e ordre en fonction du déplacement (par rapport au point de symétrie voisin) et de la déformation du réseau (par rapport au réseau cubique associé). Comme application, les coefficients du développement sont calculés pour toutes les structures du type de celles du BaTiO₃ (quadratique, orthorhombique et rhomboédrique).

Abstract. — A general method is given for calculating the electrostatic field in the neighborhood of every symmetry point of any pseudo-cubic crystalline sublattice the sites of which are occupied by identical charges. A superposition of such sublattices may be, for some statical and dynamical calculations (particularly in a shell-model framework), an useful image of an ionic crystal. The field is developed to the 3rd order in displacement (respect to the neighbouring symmetry point) and lattice strain (respect to the associated cubic lattice). As an application, the development coefficients are evaluated for all the BaTiO₃ structure-types (tetragonal, orthorhombic and rhombohedral).

1. Introduction. — Since Slatter's paper [1] it has been recorded [2 to 19] a regain of interest on calculations of local electrostatic field because of their usefulness in quantitative statitical or dynamical considerations on ferroelectricity, piezoelectricity, electro-optics, etc., in crystals having an important ionic behaviour. Particularly in any shell-model theory, the local electrostatic field should be handled with precision. Present paper is an attempt to improve and extend existing calculations by : a) taking into account the lattice-strain contribution ; b) considering the contribution of terms (in Taylor's development of the field) higher than those corresponding to a set of point dipoles located at the symmetry points of the crystal ; c) considering also other than tetragonal phases. Point (a) has already been payed much attention [7 to 18] and recently [19] we made a calculation of tetragonal BaTiO₃ and PbTiO₃ birefringences where importance of point (a) was confirmed and importance of point (b) recorded, even for a simple ionic model. Attention payed here to point (c) is due to the increasing amount of experimental information on other than tetragonal phases. In section 2 we describe a method for calculating the electrostatic field in the neighborhood of every symmetry point of any pseudo-cubic crystalline sublattice whose sites are occupied by identical point charges. This method furnish immediately, by adding the fields on a given sublattice due to all the others, the total local field on the given sublattice of any pseudo-cubic ionic crystal decomposable in sublattices located eachone near a symmetry position of every single one of the others. It is worth while to clear up that for evaluating each sublattice contribution (to the total field on the given sublattice) its effective charge q and actual displacement δ (**)(*) (respect to the associated actual symmetry point of the given sublattice) must be used. In this section we describe also general characteristics of a 3rd order (in lattice strain and sublattice displacement) development of the field.

In section 3 we apply this method to all the BaTiO₃ structure-types and evaluate all the corresponding development coefficients.

(*) Now at the Service de Physique des Solides et de Résonance Magnétique, C. E. N. Saclay, 91, Gif-sur-Yvette, France.

(**) Actually δ used in this paper is the dimensionless reduced displacement (expressed in units of the crystalline parameters)
2. Field calculation method. — 2.1 CUBIC SUBLATTICE. — Let us consider a simple cubic sublattice with a parameter $a^*$ and a charge $q$ on each site. The positions of charges, respect to a given point in the neighborhood of a symmetry point (cube corner, cube center, edge center and face center), are given by

$$ R = a^*[(l + \delta_1)i + (m + \delta_2)j + (n + \delta_3)k] ,$$

where $(l, m, n)$ are integral or half-integral numbers (this depends on the neighboring symmetry point), $(i, j, k)$ are the unitary vectors of the unit cell, and $(\delta_1, \delta_2, \delta_3)$ are small relative to unity. So the field's $z$-component at the given point is:

$$ E_z = E_z \mathbf{k} = -\sum_{l, m, n} \frac{R \cdot k}{R^3} ,$$

where $(l, m, n)$ run over all the sublattice sites (term $l = m = n = 0$ must obviously be excluded from this and similar sums). Because of symmetry, $E_z$ vanishes at every symmetry point ($\delta = 0$). If $E_z$ is developed to the $3^{rd}$ order in displacement, a dipole term (in the form $qb_3$) and octopole terms (in the form $qb_3 \delta_1 \delta_2$) where $k$ and $k'$ take in general the values 1, 2, 3) are obtained. To calculate the development coefficients, we divide, following Lorentz, the sublattice in two regions by the condition $l^2 + m^2 + n^2 \leq N^2$ (already used in [19]) which determines a sphere whose radius is $Na^*$, where $N$ is an integer. The inside-dipoles contribution $E_z^M$ is treated microscopically and the outside-dipoles contribution $E_z^M$ macroscopically, and it holds $E_z = E_z^M + E_z^M$. The macroscopic contribution is given by the Lorentz result

$$ E_z^M = \frac{4 \pi}{3} P_z = \frac{4 \pi}{3} \frac{aq_3}{a^*} .$$

2.2 PSEUDO-CUBIC SUBLATTICE. — Let us assume now that the sublattice has a pseudo-cubic deformation. The new unit cell vectors $'(i', j', k')$ are related to the old ones by

$$ i' = (l + t_{11})i + t_{12} j + t_{13} k ,$$

$$ j' = t_{21} i + (1 + t_{22}) j + t_{23} k ,$$

$$ k' = t_{31} i + t_{32} j + (1 + t_{33}) k ,$$

where $t_{ij} \leq 1$. The positions of charges are still given by $(l, m, n)$ (where $(i, j, k)$ must be replaced by $(i', j', k')$).

3. Application to the BaTiO$_3$ structure-types. — 3.1 TETRAGONAL. — Let us suppose the following lattice strain

$$ i' = (1 + t_{11})i ,$$

$$ j' = (1 + t_2) j ,$$

$$ k' = (1 + t_3) k .$$

Then we obtain for the microscopic contribution

$$ E_z^M = \frac{q}{a^*} [T_0 + T_1(t_{11} + t_2) + T_2 t_3 + T_3(t_{12}^2 + t_{13}^2) + T_4 t_3^2 + T_5 t_1 t_3 + T_6(t_{13} t_2 + t_{12} t_3) + T_7(\delta_1^2 + \delta_2^2) + T_8 \delta_3^2] \delta_3,$$

where the $T$ are dimensionless sums over $(l, m, n)$ and are easily obtained from the $K$ of [19]. Their evaluations appear in Table I. (X, Y, Z) correspond
to the associated symmetry point coordinates in the
unit cell). The macroscopic contribution is given by

\[ E_M^z = \frac{q a^2}{a^3} \left[ \frac{4 \pi}{3} - \frac{4 \pi}{5} \left( t_1 + t_2 \right) - \frac{16 \pi}{15} t_3 + \frac{16 \pi}{35} \left( t_1^2 + t_2^2 \right) + \frac{24 \pi}{35} t_3^2 + \frac{4 \pi}{7} t_1 t_2 + \frac{32 \pi}{35} \left( t_1 + t_2 \right) t_3 \right] \delta_3. \]

The \( x \)-and \( y \)-components of \( E^m \) and \( E^M \) may be
obtained from \( E^m_z \) and \( E^M_z \) by \((t_1, t_2, t_3)\) and \((\delta_1, \delta_2, \delta_3)\)
cyclic permutations. For the treatment of a tetragonal
structure we must obviously impose \( t_1 = t_2 \). The
strain parameters are then related to the usual tetra-
gonal crystalline parameters \( a \) and \( c \) by

\[ t_1 = t_2 = a/a^* - 1 \quad \text{and} \quad t_3 = c/a^* - 1, \]

where \( a^* \) is the parameter of an arbitrary associated cubic lattice.

We may choose \( a^* \) to be the parameter (obtained
by thermal extrapolation) the structure would have
if it was still cubic at the temperature of interest.

Another possible choice is \( a^* = a \), hence \( t_1 = t_2 = 0 \)
and \( t_3 = c/a - 1 \). To visualize the way of using the
results of this paper let us consider the tetragonal
phase of BaTiO3 at room temperature [20]: its
crystalline parameters are \( a = 3.992 \) Å and \( c = 4.036 \) Å
(which allows for \( t_1 = t_2 = 0 \) and \( t_3 = c/a - 1 \)), and

\[ O_4 (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \delta_{31}), \quad \text{and} \quad O_4 (\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \delta_{31}) \]

where \( \delta_{31} = 0.013 \),

\[ \delta_{34} = -0.023 \quad \text{and} \quad \delta_{34} = -0.013. \]

Replacing these values in the above expressions for
\( E^m \) and \( E^M \) we may obtain (assuming we know the
ionic charge associated to each sublattice) the
contribution (to the field at the Ba positions) of each sublat-
tice.

### Table II

<table>
<thead>
<tr>
<th>XYZ</th>
<th>( O_{x4} )</th>
<th>( O_{x9} )</th>
<th>( O_{x10} )</th>
<th>( O_{x11} )</th>
<th>( O_{z4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0, 0</td>
<td>0.359</td>
<td>9.336</td>
<td>—</td>
<td>22.622</td>
<td>5.385</td>
</tr>
<tr>
<td>0, 0, ( \frac{1}{2} )</td>
<td>0.702</td>
<td>8.213</td>
<td>—</td>
<td>15.418</td>
<td>9.220</td>
</tr>
<tr>
<td>0, ( \frac{1}{2} ), 0</td>
<td>98.348</td>
<td>45.919</td>
<td>—</td>
<td>132.246</td>
<td>5.511</td>
</tr>
<tr>
<td>( \frac{1}{2} ), 0, 0</td>
<td>—</td>
<td>113.941</td>
<td>45.919</td>
<td>—</td>
<td>132.246</td>
</tr>
<tr>
<td>0, ( \frac{1}{2} ), ( \frac{1}{2} )</td>
<td>39.216</td>
<td>14.870</td>
<td>—</td>
<td>7.956</td>
<td>36.655</td>
</tr>
<tr>
<td>( \frac{1}{2} ), 0, ( \frac{1}{2} )</td>
<td>—</td>
<td>29.294</td>
<td>14.870</td>
<td>—</td>
<td>7.956</td>
</tr>
<tr>
<td>( \frac{1}{2} ), ( \frac{1}{2} ), 0</td>
<td>30.657</td>
<td>—</td>
<td>49.318</td>
<td>146.014</td>
<td>1.940</td>
</tr>
<tr>
<td>( \frac{1}{2} ), ( \frac{1}{2} ), ( \frac{1}{2} )</td>
<td>—</td>
<td>23.165</td>
<td>—</td>
<td>15.097</td>
<td>8.588</td>
</tr>
</tbody>
</table>

### 3.2 ORTHORHOMBIC.

— Let us suppose the following lattice strain

\[ \mathbf{i}' = (1 + t_1) \mathbf{i} + t_2 \mathbf{j}, \quad \mathbf{j}' = t_2 \mathbf{i} + (1 + t_3) \mathbf{j}, \quad \mathbf{k}' = (1 + t_3) \mathbf{k}. \]

Then we obtain for the macroscopic contribution

\[ E_M^x = \frac{q a^2}{a^3} \left[ O_{x0} + O_{x1} t_1 + O_{x2} t_3 + O_{x4} t_1^2 + O_{x5} t_2^2 + \right. \]

\[ + O_{x6} t_1^2 + O_{x7} t_3 + O_{x8} (\delta_1^2 + \delta_2^2) + O_{x8} \delta_3^2 \]

\[ \left. \delta_3 \right. \]

Comparing with tetragonal case, the following
relations are obtained : 

\[ O_{x0} = T_0 \quad O_{x1} = 2T_1 \quad O_{x2} = T_2 \quad O_{x3} = 2T_3 + T_5 \]

\[ O_{x4} = T_4 \quad O_{x5} = 2T_6 \quad O_{x6} = T_7 \quad O_{x7} = 0 \quad O_{x8} = T_8 \quad O_{x9} = T_7. \]

The evaluations of the rest of the \( O \) appear in
Table II. The macroscopic contribution is given by

\[ E_M^x = \frac{q a^2}{a^3} \left[ \frac{4 \pi}{3} - \frac{8 \pi}{5} t_1 - \frac{16 \pi}{15} t_1 t_3 + \frac{52 \pi}{35} t_1^3 + \right. \]

\[ + \frac{12 \pi}{35} t_1^2 t_2 + \frac{16 \pi}{35} t_2 + \frac{24 \pi}{35} t_3 + \frac{64 \pi}{35} t_1 t_3 \left. \delta_3 \right. \]

\[ \delta_3 \]

Replacing these values in the above expressions for
\( E^x \) we may obtain (assuming we know the
ionic charge associated to each sublattice) the
contribution (to the field at the Ba positions) of each sublat-
tice.

### Table II

<table>
<thead>
<tr>
<th>Microscopic contribution's coefficients (orthorhombic case)</th>
<th>( O_{x4} )</th>
<th>( O_{x9} )</th>
<th>( O_{x10} )</th>
<th>( O_{x11} )</th>
<th>( O_{z4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0, 0</td>
<td>0.359</td>
<td>9.336</td>
<td>—</td>
<td>22.622</td>
<td>5.385</td>
</tr>
<tr>
<td>0, 0, ( \frac{1}{2} )</td>
<td>0.702</td>
<td>8.213</td>
<td>—</td>
<td>15.418</td>
<td>9.220</td>
</tr>
<tr>
<td>0, ( \frac{1}{2} ), 0</td>
<td>98.348</td>
<td>45.919</td>
<td>—</td>
<td>132.246</td>
<td>5.511</td>
</tr>
<tr>
<td>( \frac{1}{2} ), 0, 0</td>
<td>—</td>
<td>113.941</td>
<td>45.919</td>
<td>—</td>
<td>132.246</td>
</tr>
<tr>
<td>0, ( \frac{1}{2} ), ( \frac{1}{2} )</td>
<td>39.216</td>
<td>14.870</td>
<td>—</td>
<td>7.956</td>
<td>36.655</td>
</tr>
<tr>
<td>( \frac{1}{2} ), 0, ( \frac{1}{2} )</td>
<td>—</td>
<td>29.294</td>
<td>14.870</td>
<td>—</td>
<td>7.956</td>
</tr>
<tr>
<td>( \frac{1}{2} ), ( \frac{1}{2} ), 0</td>
<td>30.657</td>
<td>—</td>
<td>49.318</td>
<td>146.014</td>
<td>1.940</td>
</tr>
<tr>
<td>( \frac{1}{2} ), ( \frac{1}{2} ), ( \frac{1}{2} )</td>
<td>—</td>
<td>23.165</td>
<td>—</td>
<td>15.097</td>
<td>8.588</td>
</tr>
</tbody>
</table>
$E^\text{m}_y$ and $E^\text{M}_m$ may be obtained from $E^\text{m}_x$ and $E^\text{M}_x$ by $(\delta_1, \delta_2)$ permutation.

The strain parameters are related to the usual orthorhombic crystalline parameters $a$, $b$ and $c$ by $t_1 = (a + b)/2 \sqrt{2} a* - 1$, $t_2 = (a - b)/2 \sqrt{2} a*$ and $t_3 = c/a* - 1$. We may again extrapolate (as indicated for the tetragonal case) a value for $a*$, or we may adopt an arbitrary value, for example $a* = c$ which implies a vanishing $t_3$.

3.3 RHOMBOHEDRAL. — Let us suppose the following lattice strain:

$$
\begin{align*}
& i' = (1 + t_1) i + t_2 j + t_2 k, \\
& j' = t_2 i + (1 + t_1) j + t_2 k, \\
& k' = t_2 i + t_2 j + (1 + t_2) k.
\end{align*}
$$

Then, we obtain for the microscopic contribution

$$
E^\text{m}_x = \frac{q}{a*^2} \left[ R_0 + R_1 t_1 + R_2 t_2 + R_3 t_3^2 + R_4 \delta_3^2 + R_5 \delta_3 + R_6 (\delta_1^2 + \delta_2^2) \right] \delta_3 + \frac{q}{a*^2} \left[ R_0 t_1 + R_7 t_2^2 + R_9 t_1 t_2 \right] (\delta_1 + \delta_2).
$$

Comparing with the tetragonal case, the following relations are obtained:

$$
\begin{align*}
R_0 &= T_0, & R_1 &= - 2 T_0, & R_2 &= 3 T_0, \\
R_4 &= T_8, & R_5 &= T_7.
\end{align*}
$$

The evaluations of the rest of the $R$ appear in Table III. The macroscopic contribution is given by

$$
E^\text{M}_x = \frac{q}{a*^2} \left[ \frac{4 \pi}{3} - \frac{8 \pi}{3} t_1 + 4 \pi t_1^2 + 4 \pi t_2^2 \right] \delta_3 + \frac{q}{a*^2} \left[ - \frac{8 \pi}{5} t_2 + \frac{24 \pi}{5} t_1 t_2 + \frac{52 \pi}{35} t_2^2 \right] (\delta_1 + \delta_2).
$$

The $x$- and $y$-components of $E^\text{m}_y$ and $E^\text{M}_y$ may be obtained from $E^\text{m}_x$ and $E^\text{M}_x$ by $(\delta_1, \delta_2, \delta_3)$ cyclic permutation.

The strain parameters are related to the usual rhombohedral crystalline parameters $a$ and $\alpha$ (in our notation $a = a* \mid i' \mid$ and $\alpha$ is the angle $(i', j')$) by:

$$
\begin{align*}
t_1 &= \frac{a}{3 a*} \left[ (1 + 2 \cos \alpha)^{1/2} + 2 \sqrt{2} \sin \frac{\alpha}{2} \right] - 1, \\
\frac{t_2}{a} &= \frac{a}{3 a*} \left[ (1 + 2 \cos \alpha)^{1/2} - 2 \sqrt{2} \sin \frac{\alpha}{2} \right].
\end{align*}
$$

An useful choice for $a*$ may be $a* = a \sqrt{2} \sin \alpha/2$ which simplifies the above expressions:

$$
\begin{align*}
t_1 &= t_2 = \frac{1}{3} \left[ (1 + 2 \cos \alpha)^{1/2} - 1 \right].
\end{align*}
$$

Acknowledgements. — We are greatly indebted to Professor L. Godefroy for stimulating this work and making comments on the manuscript.

References